Patented Jan. 19, 1932 1,842,200

UNITED STATES PATENT OFFICE

JOHN HUMPHREYS RAMAGE, OF BLOOMFIELD, NEW JERSEY, ASSIGNOR TO WESTINGHOUSE LAMP COMPANY, A CORPORATION OF PENNSYLVANIA

METHOD OF DEGASIFYING METAL BODIES

No Drawing. Application filed May 4, 1928. Serial No. 275,260.

This invention relates to the art of metallurgy and more particularly relates to the art of preparing metal bodies in a substantially gas free condition so that they may be useful in the manufacture of incandescent lamps, thermionic valves of all types, X-ray and cathode-ray tubes, gas-filled electrical discharge devices, etc., wherein these metal parts are used as an incorporated part thereof.

In the lamp manufacturing industry it is customary to effect substantial degasification of the metal parts incorporated within the device by prolonged baking procedures in a high vacuum. This is usually accomplished while the assembled device is being exhausted on the pumps and when the baking of the metal parts has progressed to the point where no further gas is eliminated the device is sealed off and removed from the pumps.

With the advent of radio tubes it became necessary to remove residual gases remaining behind in the evacuated envelope after sealing off by the use of suitable so-called "getter" materials which are highly reactive metallic bodies which may be readily vaporized and caused to combine with the residual gases of the device. In spite of these precautions it is found that even with the most careful normal baking procedures the metal parts of these electrical devices progressively give off gas during the operating life of the device and thereby effectually shorten the same.

In the production of thermionic valves of the power tube type, X-ray and cathode-ray tubes, successful operating efficiency depends upon the obtaining and maintaining of a high vacuum and the complete degasification of metal parts in these tubes becomes a large problem.

The normal operating vacuum of the average radio tube is of the order of .0007 mm. of mercury pressure. The normal operating vacuum of the usual X-ray and cathode-ray tube is of the order of .00006 mm. of mercury pressure. It is appreciated that it requires very little gas evolution from the metal parts of the device to substantially destroy such a high vacuum.

In the production of lamps and electron discharge devices wherein there is intentionally added to the device a certain desired pure gas content, it is appreciated that the life and efficiency of these devices are also dependent upon maintaining a high degree of purity in the gas content.

The character of the gas content of metal bodies which is given off under these conditions is not entirely clear to science. There have been recognized at least three broad types of gaseous impurities in metal bodies, (1) entrapped or mechanically held gases, (2) combined gases, and (3) occluded or absorbed gases.

It is one of the objects of this invention to provide a method of treating metal bodies so that they may be substantially degasified.

It is another object of this invention to effect substantial removal from metal bodies that type of gaseous contamination coming under the general heading "combined gases".

Another object of this invention is to substantially remove from the surface area of the metal, those compounds contained within the metal body which are substantially vaporizable, or which have a dissociable or decomposible component which would be substantially vaporized under the operating conditions of the device.

Another object of this invention is to provide a method of substantially replacing the normal gas content of the metal body with a gas content which is either inert with respect to the metal body or which is in effect reducing with respect towards the compounds of the metal body, and which gas is of such low density that it may be more easily removed from the metal body than the normal gas content of the metal.

Another object of this invention is to provide a gas or a gas mixture which is substantially suitable to use in the practice of my invention.

Another object in this invention is to provide a useful homogeneous gas content in metal bodies which may be subsequently either evacuated when desired or made use of in some manner as in sealing-in.

Other objects and advantages of my invention will become apparent as the process is more fully disclosed.

Recently it has been found that most metals contain relatively large quantities of gases, some of which can be removed by properly scavenging the metal before casting, some of which may be removed by proper heat-treatment of the metal in vacuo, and some of which resists all efforts to remove by any known methods but which is slowly evolved when that particular metal is placed in an evacuated device and made an electrode in an electron discharge device.

The complete elimination of the deleterious effects accompanying the slow evolution of gases from any source during the operating life of an electron discharge device is most important.

During the operating life of an electron discharge device, the combined gases or intermetallic compounds such as carbides, sulfides, phosphides, oxides, hydrides, nitrides, etc., are subjected to a decomposition process under the influence of electronic bombardment in combination with a usual local heating effect and the reduced pressures usually present in such devices. The decomposition of these non-metallic constituents, the subsequent ionization or vaporization of the volatile constituent and migration to the filament or hot cathode effectually neutralizes or combines with the active constituent of the cathode and destroys the active source of the electron stream, thereby shortening the life of the device. In addition to this source of gas, the metal parts of the device also progressively eliminate an adsorbed or absorbed gas content which has been insufficiently eliminated during the baking process.

Careful experimental analysis of the gas content of various metals indicate that all metals to a great extent tenaciously retain as adsorbed or absorbed gases, hydro-carbons, oxygen, nitrogen, carbon-monoxide, carbon-dioxide and hydrogen in varying amounts. It is apparent that the diffusion rates of these gases into and out of a solid metal body is dependent not only upon the density and temperature of the metal body through which it diffuses, but is also dependent in large measure upon the densities and diffusibilities of the individual gases. Nitrogen has a density of .96737 (air=1.0), oxygen 1.1, carbon-monoxide .9670 and carbon-dioxide 1.53, whereas hydrogen has a density of only .069 (air=1), and helium has a density of only .1368 (air=1). Most metals are permeable to gases at elevated temperatures, the degree of permeability depending upon the relative densities of the metal and gas, the particular temperature employed and the size of the metal body.

According to my invention a means is provided of effecting the substantial removal of combined gases and volatile metalloidal impurities within the metal body and to effect a substitution of the normal gas content of the same with a more easily diffusing and removable gas or gas mixture such as hydrogen, helium or any hydrogen-helium gas mixture.

Metal parts treated by my process will be found to degasify in vacuo more quickly and completely than metal parts untreated by my process owing to the greater diffusibility of the substituted gas over the original adsorbed or absorbed gas content of the metal body. By judicious use of the particular gas or gas mixture employed, the residual gases which may be subsequently eliminated during the operating life of the device, may be of such nature that they may be useful in the operating efficiency of the device or may be substantially removed by the getter material incorporated within the device.

Specifically my process is directed to the use of a reducing and substituting medium comprised of hydrogen and helium, either singly, in sequence, alone, or as proportionate mixtures, as a means of effecting the main objective of my invention.

Specifically my process is also directed to the use of those metals whose compounds with oxygen, nitrogen, carbon, phosphorus and sulphur may be substantially reduced by hydrogen. Tungsten, molybdenum, nickel, chromium, iron, copper and the alloys of these metals with themselves and with other metals fall within this general classification.

More specifically this process is directed to nickel and the nickel alloys, which constitute the bulk of the metallic parts employed in the construction of incandescent lamps, electron discharge devices, gas rectifier tubes, and the like, such as plate (anode) material, grid wires, lead-in wires, supports, and as a base material for the oxide coated type filament.

As a specific embodiment in the practice of my invention in the treating of nickel or nickel alloys by my process, I subject the nickel or nickel alloy to the action of especially pure dry hydrogen, at a predetermined temperature at which the bulk of the combined impurities such as carbides, oxides, nitrides, sulfides, phosphides, etc., are reduced and converted into volatile compounds such as hydrocarbons, moisture, hydrogen-sulphide, volatile phosphides, etc., in which form they are substantially eliminated from the metal body. The heating is continued in the pure dry atmosphere of hydrogen until the metal has become substantially permeated throughout with the hydrogen gas, thereafter the metal is permitted to cool to room temperature in the hydrogen gas atmosphere without intervening exposure to any other gas.

In the treatment of nickel and nickel alloys by my process, I preferably use the finished metal article such as the plate, grid, lead wire, etc., which is ready for assembly into the electrical device. It must be ap-

preciated that such a metal article is necessarily relatively thin in diameter to the other dimensions, and as such lends itself admirably to the specific purpose of my invention.

I have determined that commercial nickel and nickel alloys contain variable amounts of the three classes of gas impurities, depending in part upon the particular method of manufacture, the alloyed components, method of fabrication, etc., and that therefore each lot of metal often must be treated differently.

It is obvious also that to effect substantial reduction of contained oxide, or contained carbide would require a different reducing temperature than that temperature which might be used in effecting the reduction of contained sulfide or phosphide, for instance.

This condition is demonstrated in the required temperatures to effect substantial reduction of contained impurities in commercial so-called pure nickel containing low determinable quantities of impurities and magno-nickel, for instance, which contains approximately 5 per cent of manganese. In the former a temperature of approximately 700° C. is required to effect removal of the bulk of the impurities contained therein whereas with the latter a temperature of only 550° C. is required over the same time interval. While the exact reason for this variance is at present unknown, it is believed to be due to the fact that the manganese has previously effected a deoxidizing and cleaning effect on the nickel to which it is added when in the molten state before casting. There may be other factors involved, however, of which we are at present unacquainted. Nickel-iron alloys, nickel-steels, etc., require a relatively high temperature to effect removal of the decomposable constituents which in the case of these alloys appear to be principally combined carbon. Each alloy employed requires a very special minimum temperature to effect the removal of combined impurities which must be predetermined for each alloy.

I have also determined that in addition to the factor of variable components effecting the minimum temperature to which the article may be heated, a major factor involved is that of degree of purity of the reducing atmosphere.

Heretofore, in the arts it has been the practice to use hydrogen to effect substantial reduction of the various reducible compounds of metals. Many processes specify pure hydrogen. Most processes contemplate the performance of the reducing action in a so-called "continuous" manner, that is, by continuously feeding into the stream of hydrogen articles or compounds which are to be reduced or treated.

The prior art has not appreciated fully that such a procedure is extremely detrimental to the proper maintenance of a substantially high degree of purity or dryness in the hydrogen atmosphere, even with the use of a very strong free flow. This is probably not fully appreciated until experiment is made wherein quantities of impurities not chemically or microscopically identifiable in relatively a large volume of metal, become active and destructive in effect when the metal is incorporated in a lamp and electron discharge device and subjected to the physico-chemical reducing effects produced therein during the operating life of the device. Surface films of oxide on a metal plate are sufficient to destroy within a few seconds the electronic activity of a hot cathode. Bare traces of a sulfide compound contained in the lead wires or plate of an electron discharge device will be decomposed and the sulfur content destroy the efficiency of an oxide-coated hot cathode. The presence of any combined nitrogen in a plate or grid material will be sufficient to substantially alter the vacuum in a highly exhausted electron discharge device, and which, because of its relative inertness, in a vapor state is not usually taken up by the getter material enclosed within the envelope of the device.

In the practice of my invention I have found that during the reducing or eliminating step I must observe two precautions (1) an extremely high degree of purity in the reducing gas, and (2) the reducing or eliminating procedure must be conducted in what might be termed a "non-continuous" manner. In the subsequent step of my process where I substantially replace the normal gas content of the metal body with the lighter and more diffusible gas atmosphere, I must substantially protect the metal body from exposure to the air until the metal has been cooled to room temperature. I therefore prefer to practice the two steps in one and the same operation and to perform the same in a chamber hermetically sealed as regards atmospheric contamination, but having provision therein for means of conducting a strong free flow of pure dry hydrogen over the heated metal parts. External means of heating the chamber is preferably employed such as by resistance wire wound furnace heated by the passage of an electric current. Heating by burning hydrocarbon vapors such as oil, gas, coal, coke, etc., should be avoided, as it is appreciated that these vapors would penetrate the metal of the chamber in sufficient quantity to contaminate the atmosphere of the same.

The method I employ in purifying the hydrogen is to substantially subject the gas to great pressure to effect partial purification of the same, and after passing through preheaters designed to remove oxygen, nitrogen, hydrocarbons, and the like, the gas is passed over a series of driers of caustic pot-

ash (KOH), a phosphorus pentoxide (P_2O_5) and then through a liquid air trap to remove the last traces of moisture impurities. This gas is then passed directly into the treating chamber used in my process.

The time interval employed in my process is in part dependent upon the particular metal part being treated, that is, upon the size of the metal part being treated. With standard dimensional articles such as are contemplated as falling within the immediate scope of the specific embodiment of my process, I find that complete elimination of these combined impurities are not obtained short of approximately four hours.

Subsequent to the elimination of the combined impurities by the action of the reducing gas at the predetermined temperature, the temperature of the chamber is permitted to slowly drop to room temperature while maintaining at all times an atmosphere of pure dry hydrogen in a strong free flow. To this gas may be added another gas component inert with respect to the metal body contained in the heated chamber, or the reducing gas (hydrogen) may be replaced entirely by such gas, which must be lighter with respect to the air or the usual or normal gas content of the metal. I have specified helium which is next to hydrogen as regards to density but at present is too commercially expensive to use, except in limited amounts for some special purposes. In the event of the substitution of such gas (helium) the metal must be held in the atmosphere of the gas at a bright red heat for a sufficient period of time to effect absorption and penetration of the gas throughout the metal body.

Having broadly outlined the scope of my invention and discussed in detail the inventive idea involved, and specifically directed the invention to the degasifying of nickel and nickel alloys, I will now describe the specific details of the process I employ in degasifying substantially pure nickel parts for radio tubes such as plates, supports, grids, etc.

The metal parts, plates, grids or support wires which are to be treated are preferably in their finished fabricated form such as stamped plates, wound grids, or finished drawn wires of the sizes required to wind the grid, or to seal into presses as support wires.

These parts are placed in metal boats, preferably also of nickel, molybdenum, or refractory nickel alloy, which also forms compounds which are reducible by hydrogen, and the boat and contents suitably incorporated in the hermetically sealed chamber of a furnace of the type previously described. A strong free flow of the especially purified dried hydrogen is passed through the chamber, the exit orifice preferably is connected to a hydrogen reservoir chamber to prevent any back diffusion of the atmosphere into the treating chamber.

The exterior heating is applied to the chamber until the temperature of the body of the chamber and the contents has been raised to approximately 700° C. Suitable temperature recording pyrometers should be employed to determine this temperature. This temperature is maintained for a period of about four hours, after which the heat source is removed and the chamber and contents permitted to cool to room temperatures. A strong free flow of hydrogen should be maintained at all times through the chamber. When the chamber has cooled to room temperatures the metal parts are removed from the chamber and are ready to be incorporated into lamps and radio tubes.

To prevent undue surface oxidation and absorption of atmospheric gases, greases from handling etc., these metal parts should be mounted and incorporated into such devices as expeditiously as possible.

Nevertheless, such a treatment and saturation with pure dry hydrogen prevents any more than surface absorption of atmospheric gases over a prolonged period of time at room temperatures. Exposure of such treated parts for a period of three months to atmospheric conditions has not apparently altered the gas content of the parts.

When the material to be treated is an alloy of nickel-iron or nickel-manganese, the temperature of the process only is varied. Nickel-iron alloys are heated to approximately 800° C. to 850° C. whereas nickel-manganese alloys containing approximately 5 per cent manganese may be heated to only 550° C.

One of the specific results of the practice of my invention is in the treatment of "spuds", so-called because they are supports for various parts of the electrical device, which parts are mounted into the press of the device but which do not themselves carry any electrical currents, nor do they extend through the press of the device and therefore require the use of a metal essentially forming gas tight or hermetic seals with the glass of the device.

Extreme difficulty initially was encountered in using as "spud" material, wire which was sufficiently soft and pliable to work easily and which would be weldable, and at the same time have a coefficient of expansion close to that of the glass employed in the seal to permit a non-cracking seal to be obtained. Many materials have been tried out. The development of continuous feed spud-stem making machines enhanced this trouble and it was found that the normal gas content of the nickel or nickel alloys employed were sufficient so that on sealing into the press, the gas evolution from the 30 to 40 nil. wire caused a series of gas bubbles to appear which surrounded the part of the metal in the glass and caused loose adherence of the spud in the

glass of the seal. This loose adherence was undesirable in that it often resulted in the spud dropping out of position during mounting.

When this gas content was removed from the spud material by previous treatment in high vacuum, the spuds stuck to the glass but due to the wide difference in the respective coefficients of expansion, the glass of the press was subjected to intense internal strains and developed cracks.

By substituting for pure nickel, heretofore employed, a manganese alloy of nickel from which the bulk of the mechanically enclosed gases have been eliminated prior to casting through such addition of managanese and subjecting the wires formed of the alloy to my hydrogen treating process at a temperature approximating 550° C. this sealing-in trouble has been substantially eliminated. The treated alloy has had the absorbed or adsorbed gas content substantially displaced by the hydrogen, which during the subsequent sealing-in process envolves the gas into the glass of the seal in a series of extremely fine bubbles encompassing and surrounding that portion of the alloy immersed in the glass. This provides in effect a cushion comprised of minute gas bubbles interposed between the metal and the glass. The walls of glass surrounding these cushion bubbles are sufficiently elastic to take up the differences in the coefficient of expansion of the two materials, thus promoting a rigid adherent glass seal. The gas content of the bubbles is moreover, more easily compressible than the mixed gas content heretofore encountered in these metal parts.

In addition, this process has effectively removed from the metal those combined decomposible gaseous compounds such as carbide, sulfide, nitride, phosphide, etc., which were originally present. The untreated alloy does not yield this result. The completely vacuum degasified alloy does not yield this result. The alloy which has been substantially annealed by any heretofore known continuous annealing or pot-annealing method does not accomplish this purpose.

By my process which I have specifically described in its relation to nickel and nickel alloys but which is not necessarily confined to this metal or alloy, I am enabled to eliminate from the metal parts enclosed in the evacuated portion of a lamp or electrical discharge device substantially all of the contaminating normally contained and difficultly removable gaseous impurities and not heretofore removable by any other prior process. I have thereby materially increased the ease by which these lamps and electron discharge devices may be manufactured by shortening materially the exhaust period of the same, and I have furthermore, through the elimination of the decomposable intermetallic compounds, contained within the metal parts, materially increased the operating life and efficiency of these devices.

While there may be many variations of this general process which can be devised by one skilled in the art, these variations are contemplated and those which may fall within the scope of the claims are substantially anticipated.

What is claimed is:

The process of effecting substantial degasification of a metal by substituting for the normal gas content thereof a more easily removable gas, comprising heating the metal to elevated temperatures in an atmosphere of substantially pure dry hydrogen to drive out the normal gas content thereof and subsequently removing the substituted adsorbed hydrogen content in the metal by heating the metal at elevated temperatures in vacuo.

In testimony whereof I have hereunto subscribed my name this 3rd day of May, 1928.

JOHN HUMPHREYS RAMAGE.